

【国際公開パンフレット】

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

PCT

(43) International Publication Date
22 August 2002 (22.08.2002)

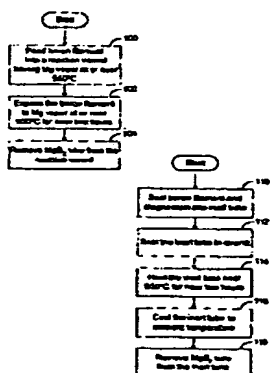
PCT

(11) International Publication Number
WO 02/064859 A2

- (51) International Patent Classification: C35C
- (11) International Application Number: PCT/US2002/00004
- (22) International Filing Date: 8 February 2002 (08.02.2002)
- (23) Filing Language: English
- (24) Publication Language: English
- (39) Priority Data: 62/591,575 15 February 2001 (15.02.2001) US
- (71) Applicant: IOWA STATE UNIVERSITY RESEARCH FOUNDATION (US); 310 Lab of Mechanics, Ames, IA 50011 (US).
- (72) Inventors: FRIEDMANN, Douglas, K; 1112 Oakford Street, Ames, IA 50014 (US); CANTFIELD, Paul, C; 806 Coyt Circle, Ames, IA 50010 (US); SERGEY, Ruslan, L; 3913 Jewell Circle, Ames, IA 50010 (US); OSTENSON, Andrew, E; 416 Westwood Drive, Ames, IA 50014 (US); PETROVIC, Gabor, J; 245 Steele Avenue, Apt. 304, Ames, IA 50014 (US); CRYNBERG, Charles, R; 800 Plaza Drive #108, Ames, IA 50014 (US); LAFFERTY, Gerald, G; 800 George Street, F-30000 Omaha (NE).
- (74) Agent: WINGATE, Kevin, L; Loyd, Vito & Meyer, Ltd., 6815 Weaver Road, Suite 300, Rockford, IL 61114 (US).
- (75) Designated States (abstract): AF, AL, AM, AN, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, FI, GB, GR, GU, HA, HK, HU, IL, IN, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, NZ, NG, NI, NO, NP, PA, PE, PG, PH, PK, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, SM, SN, SR, ST, SV, SZ, TD, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VE, VN, YU, ZA, ZM, ZW.

(Continued on next page)

(54) Title: SYNTHESIS OF SUPERCONDUCTING MAGNESIUM DIBORIDE OBJECTS



(57) Abstract: A process to produce magnesium diboride objects from boron objects with a desired form is presented. Boron objects are stacked with magnesium vapor at a predetermined time and temperature to form magnesium diboride objects having a morphology similar to the boron object's original morphology.

WO 02/064859 A2

WO 02/064859 A2 

SI, SE, SI, TI, TM, TN, TR, TT, TZ, UA, UG, UZ, VN,
YU, ZA, ZM, ZW.

Published:

— without international search report and as to be republished
upon receipt of that report

(54) Designated States (episodes): ARIPO patent (GB, GM,
KE, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZM, ZW),
European patent (AM, AZ, BY, KG, KZ, MD, RU, TR, TM),
European patent (AL, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LI, MC, NL, PT, SE, SI, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NI, SN, TD, TG).

For pre-locator codes and other abbreviations, refer to the "Guide
to the Patent on Codes and Abbreviations" appearing at the beginning
of each regular issue of the PCT Gazette.

WO 02/064859

PCT/US02/04804

SYNTHESIS OF SUPERCONDUCTING MAGNESIUM DIBORIDE OBJECTS

FIELD OF THE INVENTION

[0001] The present invention relates generally to superconductivity, and more particularly relates to a method of manufacturing superconducting magnesium diboride objects.

BACKGROUND OF THE INVENTION

[0002] The recent discovery of superconductivity in magnesium diboride (MgB_2) having a superconducting transition temperature (T_c) of approximately thirty nine degrees Kelvin (39 K) introduced a new, simple binary intermetallic superconductor having three atoms per formula unit. MgB_2 has a T_c that is higher by almost a factor of two of any known non-oxide and non- CuO -based compound. Measurements of the boron isotope effect in MgB_2 , which is an indication of the extent to which phonons mediate superconductivity, are consistent with the superconductivity being mediated via electron-phonon coupling. Measurements of the upper critical field, $H_{c2}(T)$, the thermodynamic critical field, $H_d(T)$, and the critical current, J_c , indicate that MgB_2 is a type-II superconductor with properties that are consistent with an intermetallic superconductor that has a T_c of approximately 40 K.

[0003] It is believed that MgB_2 forms via a process of diffusion of magnesium (Mg) vapor into boron grains. Superconducting wire, tape, and film can be used for research and applied purposes. For example, superconducting wire can be used for making superconducting magnets, fault-current limiters, and for power transmission. Films can be used to make Josephson junctions, SQUIDS (superconducting quantum interference devices), micro-electronic interconnects and other devices. The films can also be used to coat microwave cavities and other objects.

BRIEF SUMMARY OF THE INVENTION

[0004] It is an object of the instant invention to provide a method of manufacturing magnesium diboride wires, tapes, and films. It is a further object of the instant invention to

WO 02/064859

PCT/US02/04904

2

provide a method of manufacturing magnesium diboride wire using boron filaments and films using boron films.

[0085] In view of the above objects, it is an object of the instant invention to provide a method of manufacturing magnesium diboride wire and films utilizing simple cost effective techniques.

[0086] In accordance with an embodiment of the instant invention, a method of manufacturing magnesium diboride wire or film comprises the steps of exposing boron filaments, tape, or film to Mg vapor for a predetermined time and temperature to form MgB_2 wire, tape or film, removing the formed MgB_2 wire, tape or film from the Mg vapor, and either quenching the MgB_2 wire, tape or film to near ambient temperatures or quenching the reaction vessel to near ambient temperatures and removing the MgB_2 wire, tape or film from the reaction vessel.

[0087] In accordance with an alternate embodiment of the instant invention, a method of manufacturing magnesium diboride wire, tape or film comprises the steps of: a) sealing at least one boron filament, tape or film and magnesium into a tantalum (Ta) or similarly inert tube with excess magnesium with respect to MgB_2 ; b) protecting the tantalum from oxidation (e.g., sealing the Ta tube in quartz); c) heating the sealed Ta tube at 950 C for two hours or less for a boron filament diameter of 100 micrometers (with differing heating times and temperatures for differing thicknesses of boron used); d) quenching the Ta tube to room temperature and removing the formed magnesium diboride wire, tape or film from the Ta tube.

[0088] Other objectives and advantages of the invention will become more apparent from the following detailed description when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0089] The accompanying drawings incorporated in and forming a part of the specification illustrate several aspects of the present invention, and together with the description serve to explain the principles of the invention. In the drawings:

[0090] FIG. 1a is a flow diagram for illustrating a methodology for manufacturing magnesium diboride wire;

WO 02/064859

PCT/US02/04864

3

- [0011] FIG. 1b is a flow diagram for illustrating an alternate methodology for manufacturing magnesium diboride wire;
- [0012] FIG. 2a is a cross-sectional view of a boron filament used in the manufacturing of magnesium diboride wire;
- [0013] FIG. 2b is a cross-sectional view of magnesium diboride wire made in accordance with the teachings of the instant invention;
- [0014] FIG. 3 is an image of magnesium diboride wires made in accordance with the teachings of the instant invention;
- [0015] FIG. 4 is a graphic illustration of the magnetization divided by an applied magnetic field of 25 Oe for a zero field cooled magnesium diboride wire made in accordance with the teachings of the instant invention;
- [0016] FIG. 5 is a graphical plot illustrating the relationship between the electrical resistivity of magnesium diboride wire and temperature;
- [0017] FIG. 6 is an expanded view of the resistivity data of FIG. 5 near the superconducting transition temperature; and
- [0018] FIG. 7 is a graphic illustration of $H_c(T)$ data inferred from the resistivity data similar to that shown in figure 5; and
- [0019] FIG. 8 is a graphic illustration of the superconducting critical current density as a function of an applied field for temperatures ranging from 5K to 35K in increments of 5K.
- [0020] While the invention will be described in connection with certain preferred embodiments, there is no intent to limit it to those embodiments. On the contrary, the intent is to cover all alternatives, modifications and equivalents as included within the spirit and scope of the invention as defined by the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

[0021] While the instant invention may be used to manufacture magnesium diboride (MgB_2) objects such as MgB_2 wire, tape, and film, the instant invention will be described using MgB_2 wire. Those skilled in the art will recognize that the process used to make the MgB_2 wire can also be used to make MgB_2 film, tape or any other form or structure by turning boron having a similar morphology (i.e., form) into MgB_2 via exposure to magnesium

WO 02/064859

PC/EES02/4-0804

4

vapor. For example, boron coatings on cavities or other devices could be turned into MgB_2 coatings. Turning now to figure 1a, the steps to manufacture magnesium diboride (MgB_2) wire are shown. Boron filaments are fed into a reaction chamber or vessel (step 100). The boron filaments may be continually fed into the reaction vessel or pre-cut to a specified length. The boron filaments are exposed to Mg vapor in the reaction vessel for a predetermined time and temperature to form MgB_2 wire (step 102). The vapor pressure is determined by the reaction vessel temperature using well established vapor pressure versus temperature curves as known in the art. The minimum exposure time increases with increasing filament diameter and decreases with increasing temperature. For example, a 100 micrometer diameter boron filament that is exposed to Mg vapor heated to or near 950 C for approximately two hours forms MgB_2 wire. A 140, 200, or 300 micrometer diameter filament must be heated longer than two hours for the transformation to be completed. The 140 and 200 micrometer diameter filaments form wire when exposed to Mg vapor heated to or near 950 C for near 6 hours and the 300 micrometer diameter filaments form wire when exposed to Mg vapor heated to or near 950 C for near 15 hours. During the heating step, MgB_2 wire is formed as a result of the reaction between the boron filaments and the Mg vapor. After the MgB_2 wire has been formed, the MgB_2 wire is removed from the reaction vessel (step 104). The MgB_2 wire is quenched to near ambient temperatures or is cooled at a predetermined ramp rate.

[0022] The same process is used for other boron objects. For example, MgB_2 films are created by depositing boron film on a substrate inert to the Mg vapor such as strontium titanate. The film is deposited using pulsed laser deposition or other known methods of deposition. Once the boron film is deposited on the substrate, the film is placed or fed into a reaction vessel and exposed to Mg vapor for a predetermined time and temperature. For example, a one micrometer thick boron film that is exposed to Mg vapor heated to or near 950 C for approximately a half hour forms MgB_2 film. After the MgB_2 film is formed, the film is removed from the reaction vessel and either quenched to near ambient temperature or is cooled at a predetermined ramp rate.

[0023] Turning now to figure 1b, the steps to manufacture magnesium diboride (MgB_2) wire using an alternate embodiment are shown. Boron filaments and magnesium are placed into a tantalum (Ta) or other inert tube such as niobium, molybdenum, tungsten, and possibly iron and some steels (step 110). The nominal ratio of magnesium to boride in the Ta tube is

WO 02/064859

PCT/US02/04004

5

MgB₂. While a nominal ratio of Mg:B was used, those skilled in the art will recognize that other ratios may be used provided that there is excess magnesium with respect to MgB₂ (i.e., the ratio of Mg:B is greater than 1:2). The Ta tube is then sealed in quartz or an equivalent material to protect the Ta from oxidation at elevated temperatures (step 112). Those skilled in the art will recognize that other methods of providing such protection can be used. The sealed Ta tube is placed in a box furnace at a temperature of 950 C for approximately two hours (step 114). The Ta tube is then removed and cooled to room temperature (step 116). MgB₂ wire forms during the temperature soak at 950 C and the wire is removed when the Ta tube is near room ambient temperature (step 118).

[0024] Now that the manufacturing processes have been described, the characteristics of the MgB₂ wire formed will now be described. Turning now to figures 2a and 2b, the boron filament 200 and MgB₂ wire 210 are shown. In figure 2a, a cross-section of a boron filament 200 is shown. The boron filament diameter 202 is 100 μ m and it has a tungsten/tungsten boride core 204 having a diameter of approximately 15 μ m. The tungsten/tungsten boride core 204 is part of the boron filament 200 and does not appear to be affected by the exposure of the boron filament 200 to magnesium. As discussed hereinbelow, the tungsten/tungsten boride core 204 does not seem to effect the superconducting properties of the resulting MgB₂ wire. While a 100 μ m diameter filament was used, it should be recognized that other diameters and boron tapes may be used with appropriate changes in temperature and time of exposure to Mg vapor. Figure 2b shows a cross-section of MgB₂ wire 210 produced after steps 100-104 or 110-118 are taken. In figure 2b, the MgB₂ wire 210 has a diameter 212 of approximately 160 μ m. The increased diameter of the MgB₂ wire 210 is consistent with observations that there is an expansion associated with the formation of MgB₂ powders during synthesis.

[0025] Figure 3 shows an image of the resulting MgB₂ wire segments 300. As can be seen, there has been significant warping and bending of the boron filament 200 as a result of the reaction with the magnesium vapor at high temperature. Although the MgB₂ wire segments 300 are somewhat brittle, the integrity of the filament segments is preserved during the exposure to the Mg vapor (i.e. the boron filaments 200 do not decompose or turn into powder). The MgB₂ wire may be encased in a sleeve to increase mechanical stability of the MgB₂ wire.

WO 02/044859

PCT/US02/04004

6

[0026] Based upon a diameter 212 of 160 μm and measuring the length and mass of several MgB_2 wire segments 300, the density of the wire is determined to be approximately 2.4 g/cm^3 . This is to be compared with a theoretical value of 2.55 g/cm^3 for a single crystal sample using lattice parameters $a = 3.14 \text{ \AA}$ and $c = 3.52 \text{ \AA}$ for the hexagonal unit cell. This implies that the MgB_2 wire segments 300 are probably better than approximately 90% of the theoretical density. It should be noted that the small tungsten/hungsten boride core would come in as a roughly 10% correction, and therefore is within the level of uncertainty.

[0027] Turning now to figure 4, the temperature-dependent magnetization of MgB_2 wire is shown. The data were taken after the MgB_2 wire segments 300 were cooled in a zero magnetic field and then warmed in a field of 25 Oe (Oersteds). Taking into account the aspect ratio of the MgB_2 wire segments, a susceptibility very close to a value of $-1/4\pi$, which is the value expected for total shielding and a demagnetization factor close to zero, was obtained. The superconducting transition temperature (T_c) of 39.4 K is determined from these data by using an onset criterion (2% of $-1/4\pi$). The width of the temperature transition (10% - 90%) is 0.9 K.

[0028] Turning now to figure 5, the temperature-dependent electrical resistivity of MgB_2 wire segments 300 formed by the process of the present invention is shown. The resistivity, ρ , at room temperature has a value of 9.6 $\mu\text{Ohm-cm}$ whereas ρ at 77 Kelvin has a value of 0.6 $\mu\text{Ohm-cm}$ and ρ at 40 Kelvin has a value of 0.38 $\mu\text{Ohm-cm}$. This leads to a residual resistivity ratio of RRR equal to 25.3. The resistivity for temperatures just above T_c is lower by a factor of ten to twenty over existing superconducting materials such as Nb_3Sn . This means that the MgB_2 wire may manifest less need to be encased in a relatively higher conducting sheath (such as copper) as required by materials such as Nb_3Sn to keep wire resistance down in the event that temperature rises above the superconducting transition temperature of the material being used. It should be noted that the shape of the resistivity curve and the RRR values are qualitatively the same as the shape and RRR values observed for sintered pellets of polycrystalline Mg^{10}B_2 . The resistivity of the sintered pellet samples of polycrystalline Mg^{10}B_2 is approximately 1 $\mu\text{Ohm-cm}$ at 40 K. This somewhat higher value of the calculated resistivity for the sintered pellet samples of polycrystalline Mg^{10}B_2 is consistent with the sintered pellet sample having an actual density substantially lower than either the MgB_2 wire or the theoretical value.

WO 02/064859

PC7/US62/04804

7

[0029] The temperature-dependent resistivity shown in Figure 5 can be fit by a power law of $\rho = \rho_0 + \rho_1 T^\alpha$ with α approximately equal to 2.6 between the superconducting critical temperature, T_c , and 200 Kelvins. This is comparable to the power law $R = R_0 + R_1 T^\alpha$, with α approximately equal to 2.8, found for the sintered Mg^{10}B_2 pellet samples over a comparable temperature range. Due to the similarity of the two power laws, those skilled in the art will recognize that the resistivity of MgB_2 will not have a linear slope for temperatures between T_c and 300 Kelvins. On the other hand, using an average Fermi velocity of $v_F = 4.8 \cdot 10^7$ cm/s and a carrier density of $6.7 \cdot 10^{23}$ el/cm³ (two free electrons per unit cell) the electronic mean free path is estimated to be approximately 600 Å at T_c . This is clearly an approximate value of the electronic mean free path, but with an estimated superconducting coherence length of approximately 50 Å, these values place MgB_2 wire segments 300 well within the clean limit, which those skilled in the art will recognize as an indication of high sample quality. This indicates that superconducting properties such as the upper critical field and critical current may be improved by the judicious addition of impurities.

[0030] The superconducting transition temperature, $T_c = 39.4$ K, can be determined from both the magnetization and resistivity data shown in figures 4 and 5. This value is slightly higher than the $T_c = 39.2$ K value determined for isotopically pure Mg^{10}B_2 , but is significantly lower than $T_c = 40.2$ K for Mg^{10}B_2 . The value is consistent with an approximate 80% natural abundance of ^{10}B . It should be noted that the superconducting transition is both relatively high and sharp in the MgB_2 wire segments 300. This means that either very few impurities are being incorporated into the MgB_2 wire segments 300 or that what few impurities are being incorporated are having very little effect on either resistivity or T_c . Figure 6 shows an expanded view of the temperature-dependent resistivity data of Figure 5 near the superconducting transition temperature T_c .

[0031] The temperature dependence of the upper critical field, $H_{c2}(T)$, is illustrated in figure 7. For each field, three data points are shown. The three data points are onset temperature, temperature for maximum dp/dT , and completion temperature. Qualitatively these data are similar to the $H_{c2}(T)$ data inferred from measurements on Mg^{10}B_2 sintered pellets. Quantitatively, at an H of 9 T, the width of the resistive transition for a MgB_2 wire segments 300 is roughly half of the width found for the sintered Mg^{10}B_2 pellet samples.

WO 02/044859

PCT/US02/04804

8

These data are consistent with the wire sample being of comparable or better quality as the sintered pellet samples.

[0032] Turning now to figure 8, data on the critical current I_c is shown. The open symbols, represented generally as 400, are I_c values extracted from direct measurements of the current dependent voltage across the MgB_2 wire segment 300 at given temperature and applied field values. The filled symbols, represented generally as 402, are I_c values inferred from magnetization loops by application of the Bean model. The temperature values are incremented every 5K and range from 5K to 35K. 5K measurements and extrapolations are generally illustrated at line 404, 10K measurements and extrapolations are generally illustrated at line 406, 15K measurements and extrapolations are generally illustrated at line 408, 20K measurements and extrapolations are generally illustrated at line 410, 25K measurements and extrapolations are generally illustrated at line 412, 30K measurements and extrapolations are generally illustrated at line 414, and 35K measurements and extrapolations are generally illustrated at line 416. The dashed lines connect data sets taken at the same temperature. The direct measurement of I_c was limited to values below approximately 200 A/cm² due to resistive heating from the leads attached to the MgB_2 wire segment 300 and contact resistance. As can be seen, the extrapolations of the directly measured, low I_c data and the Bean-model-inferred, high I_c data match up moderately well. In comparison to the I_c data for a sintered pellet of $Mg^{10}B_2$, I_c for the MgB_2 wire segment 300 is roughly a factor of two higher at low fields and temperatures and over an order of magnitude higher at high fields.

[0033] A simple technique of producing low resistivity, high density, high T_c MgB_2 in wire, tape, or film form via exposure of boron filaments, tape, or film to Mg vapor has been presented. The resulting MgB_2 wire has approximately 90% the theoretical density of MgB_2 and measurements of the temperature dependent resistivity reveal that MgB_2 is highly conducting in the normal state. The room temperature resistivity has a value of 9.6 $\mu\Omega\text{-cm}$ whereas the resistivity at a temperature of 40 K is 0.38 $\mu\Omega\text{-cm}$. This means that even in the normal state, MgB_2 wires can carry significant current densities. This should be compared with the resistivity of Nb_3Sn , which has a resistivity value of 11 $\mu\Omega\text{-cm}$ at a temperature of 20K and a resistivity value of 80 $\mu\Omega\text{-cm}$ at a temperature of 300 K.

[0034] The MgB_2 wires can be used for both research and applied purposes. Examples include, but are not limited to, superconducting magnets, power transmission lines, fault-

WD 02064859

PC7/CS020/0004

9

current limiters, and micro-electronic circuits (e.g. SQUIDS or interconnects). It should be noted that boron filaments and tapes are produced in a variety of sizes and of arbitrary lengths and that different applications may require different sizes of MgB_2 wires or tapes. The conversion of boron filaments or tapes into MgB_2 wire or tapes as part of a continuous process leads to the possibility of simple manufacturing of light weight, high T_c wires or tapes with remarkably small normal state resistivities. Additionally, the process used in creating the MgB_2 wire or tape can be used to turn boron coatings on cavities or other devices into high-quality superconducting films.

[0035] The foregoing description of various embodiments of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise embodiments disclosed. Numerous modifications or variations are possible in light of the above teachings. The embodiments discussed were chosen and described to provide the best illustration of the principles of the invention and its practical application to thereby enable one of ordinary skill in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the scope of the invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally, and equitably entitled.

WO 02/064839

PCT/US02/04084

10

WHAT IS CLAIMED IS:

1. A method for producing a magnesium diboride object comprising the step of reacting a boron object with magnesium vapor at a predetermined time and temperature to form the magnesium diboride object.
2. The method of claim 1 wherein the magnesium vapor is enclosed in a reaction vessel, the method further comprising the steps of:
feeding the boron object into the reaction vessel;
removing the formed magnesium diboride object from the reaction vessel; and
cooling the magnesium diboride object at a predetermined rate.
3. The method of claim 1 wherein the boron object is boron film, the method further comprising the step of depositing the boron film on a substrate inert to the magnesium vapor.
4. The method of claim 1 wherein the boron object is a boron filament and wherein the step of reacting the boron object with the magnesium vapor at a predetermined time and temperature comprises the step of reacting the boron filament at a predetermined time and temperature.
5. The method of claim 4 wherein the boron filament has a diameter of less than approximately one hundred micrometers and wherein the step of reacting the boron filament at a predetermined time and temperature comprises the step of reacting the boron filament at a temperature of approximately 950C for a time of approximately two hours to form magnesium diboride wire.
6. The method of claim 4 wherein the boron filament has a diameter between approximately one hundred forty micrometers and two hundred micrometers and wherein the step of reacting the boron filament at a predetermined time and temperature comprises the step of reacting the boron filament at a temperature of approximately 950C for a time of less than approximately six hours to form magnesium diboride wire.
7. The method of claim 4 wherein the boron filament has a diameter of approximately three hundred micrometers and wherein the step of reacting the boron filament at a predetermined time and temperature comprises the step of reacting the boron filament at

WO 02/064359

PCT/US02/04084

11

a temperature of approximately 950C for a time of less than approximately fifteen hours to form magnesium diboride wire.

8. The method of claim 5 further comprising the step of encasing the magnesium diboride wire in a conductive sleeve.

9. A method for producing a magnesium diboride object comprising the steps of:
feeding the boron object into a reaction vessel having magnesium vapor within the reaction vessel;
reacting the boron object with the magnesium vapor for a predetermined time at a predetermined temperature;
removing the formed magnesium diboride object from the reaction vessel; and
cooling the magnesium diboride object at a predetermined rate.

10. The method of claim 9 wherein the boron object is boron film, the method further comprising the step of depositing the boron film on a substrate inert to the magnesium vapor.

11. The method of claim 10 wherein the boron film has a thickness of approximately one micronmeter and the step of reacting the boron object with the magnesium vapor for a predetermined time at a predetermined temperature comprises the step of reacting the boron film at a temperature of approximately 950 C for a time of approximately one half hour.

12. The method of claim 9 wherein the boron object is a boron filament and wherein the step of reacting the boron object with the magnesium vapor at a predetermined time and temperature comprises the step of reacting the boron filament at a predetermined time and temperature.

13. The method of claim 12 wherein the boron filament has a diameter of less than approximately one hundred micrometers and wherein the step of reacting the boron filament at a predetermined time and temperature comprises the step of reacting the boron filament at a temperature of approximately 950C for a time of approximately two hours to form magnesium diboride wire.

14. The method of claim 12 wherein the boron filament has a diameter of between one hundred forty and two hundred micrometers and wherein the step of reacting the boron

WO #2004/859

PCT/US02/04864

12

filament at a predetermined time and temperature comprises the step of reacting the boron filament at a temperature of approximately 950C for a time of less than approximately six hours to form magnesium diboride wire.

15. The method of claim 12 wherein the boron filament has a diameter of less than approximately three hundred micrometers and wherein the step of reacting the boron filament at a predetermined time and temperature comprises the step of reacting the boron filament at a temperature of approximately 950C for a time of less than approximately fifteen hours to form magnesium diboride wire.

16. A magnesium diboride wire formed by the step comprising exposing a boron filament to magnesium vapor in a reaction vessel for a predetermined time and temperature.

17. The magnesium diboride wire of claim 16 wherein a ratio of magnesium to boron is in excess of 1:2.

18. The magnesium diboride wire of claim 16 wherein the boron filament has a core comprised of a core material that is inert to magnesium vapor.

19. The magnesium diboride wire of claim 16 wherein the core material is tungsten/tungsten boride.

20. The magnesium diboride wire of claim 16 further comprising a conductive sleeve encasing the formed magnesium diboride wire.

21. A method for producing a magnesium diboride object comprising the steps of:
putting a boron object and magnesium into an inert tube;
heating the inert tube to a predetermined temperature for a predetermined time to form the magnesium diboride object;
cooling the magnesium diboride object at a predetermined rate; and
removing the formed magnesium diboride object from the inert tube.

22. The method of claim 21 wherein the magnesium diboride object is one of wire, tape, and film and wherein the step of heating the inert tube to a predetermined temperature for a predetermined time to form the magnesium diboride object comprises the step of heating the inert tube to approximately 950 C for a predetermined time to form the magnesium diboride object.

23. The method of claim 22 wherein the one of wire, tape, and film has a diameter or thickness, and wherein the step of heating the inert tube to approximately 950 C for a predetermined time to form the magnesium diboride object comprises the step of heating the inert tube to approximately 950 C for one of approximately one half hour for a diameter or thickness of one micrometer, approximately two hours for a diameter or thickness of one hundred micrometers, less than approximately six hours for a diameter or thickness of one hundred forty to two hundred micrometers, and less than fifteen hours for a diameter or thickness of three hundred micrometers to form the magnesium diboride object.

24. A magnesium diboride film formed by the steps comprising:
putting a boron film and magnesium into an inert tube;
heating the inert tube to a predetermined temperature for a predetermined time to form the magnesium diboride film;
cooling the magnesium diboride film at a predetermined rate; and
removing the formed magnesium diboride film from the inert tube.

25. The magnesium diboride film of claim 24 wherein the boron film is deposited on a substrate that is inert to the magnesium.

WO 02/064859

PCT/US02/04004

FIG. 1a

1/6

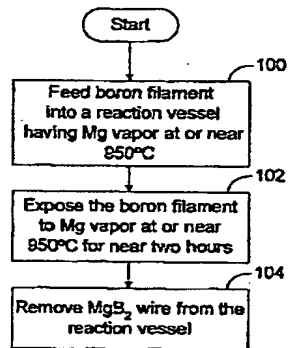
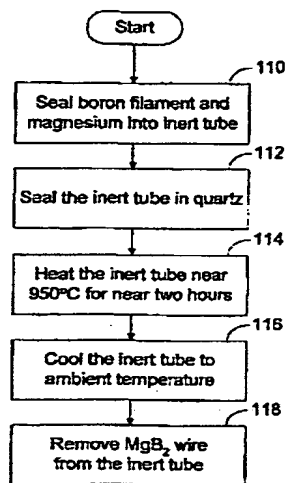


FIG. 1b



WO 02/064859

PCT/US02/01884

FIG. 2a

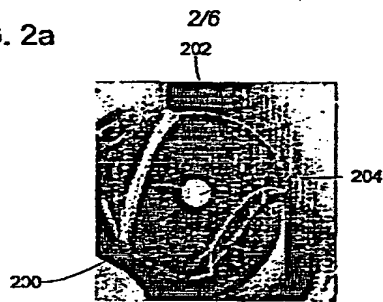
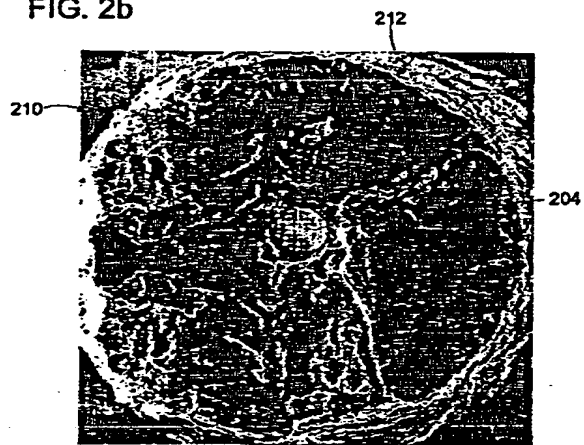


FIG. 2b



WD 82/064859

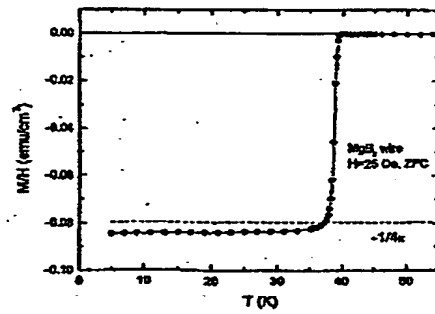
PCT/US02/64064

3/6

FIG. 3



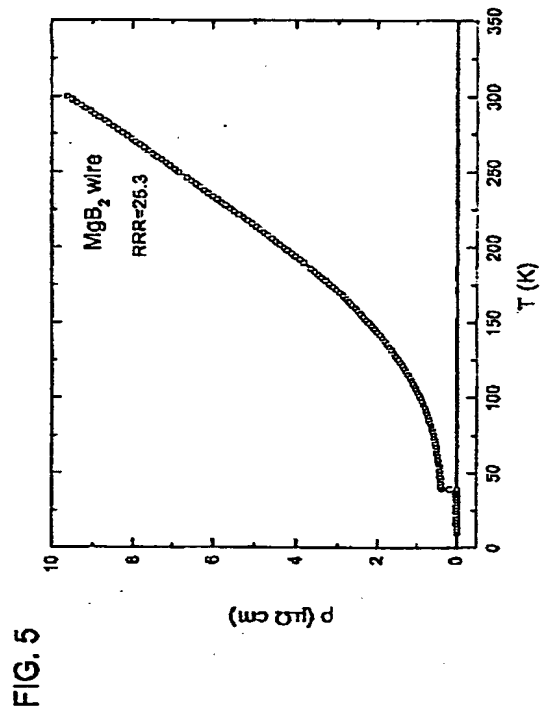
FIG. 4



WO 02/064859

PCT/US02/04064

4/6



WO 02/064859

PCT/US02/04004

5/6

FIG. 6

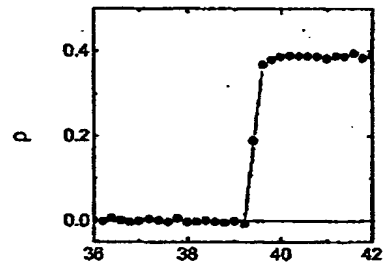
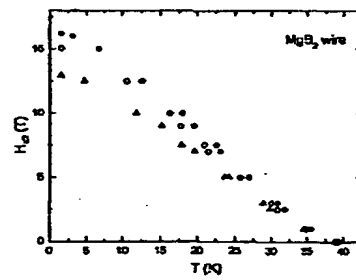


FIG. 7



WO 02/04859

PC170502/64064

6/6

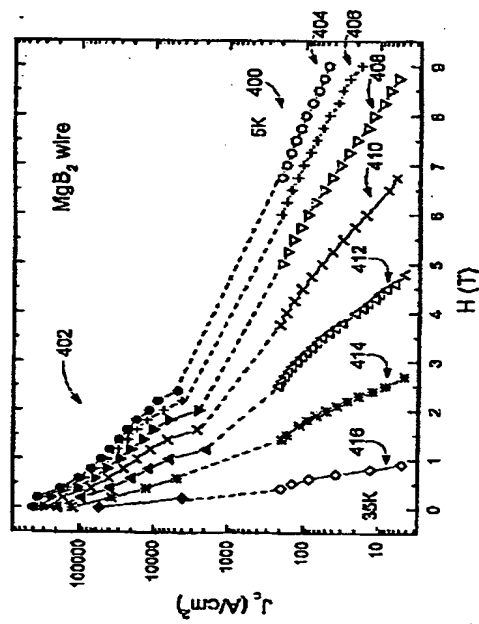


FIG. 8

【国際公開パンフレット（コレクトバージョン）】

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

PCT

(43) International Publication Date
22 August 2002 (22.08.2002)(18) International Publication Number
WO 02/064859 A3(51) International Patent Classification: B05D 5/12
C23C 14/08, H01L 3/20

(27) International Application Number: PCT/US00/0304

(22) International Filing Date: 8 February 2002 (08.02.2002)

(25) Filing Language: English

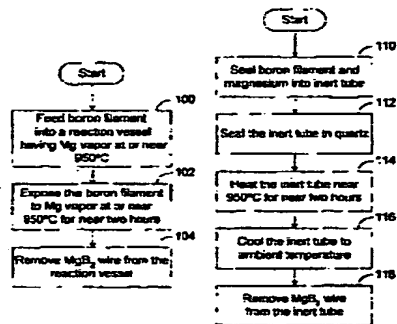
(26) Publication Language: English

(30) Priority Data: 60/269,092 15 February 2001 (15.02.2001) US

(71) Applicant: HOWE STATE UNIVERSITY RESEARCH
FOUNDATION (US); 310 Lab of Mechanics, Ames,
IA 50011 (US)(72) Inventor: FINNEWORK, Douglas, R.; 1322 Oakland
Street, Ames, IA 50014 (US); CANFIELD, Paul, C.; 808
Owens Circle, Ames, IA 50010 (US); SORACE, Paul, E.;
3913 Brookside Circle, Ames, IA 50010 (US); OSTEN-
SON, James, E.; 416 Westwood Drive, Ames, IA 50014(US) PETROVIC, Catherine, 245 Steele Avenue, Apt.
301, Ames, IA 50014 (US); CUNNINGHAM, Charles,
E. 800 Pine Drive #101, Ames, IA 50014 (US); LA PER-
TO, Girard, 66 Rue George Black, F-38000 Grenoble
(FR)(74) Agent: WINGATE, Kevin, L.; Leggett, Vot & Meyer,
P.A., 6615 Weaver Road, Suite 300, Rockford, IL 61114
(US)(75) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, FR, GB, GR,
GM, GU, HK, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MY, NZ, OM, PA, PE, PG, PH, PL, PT, RO, RU, SD, SI, SG,
SK, SL, SM, TN, TR, TT, TZ, UA, UG, UZ, VN,
YU, ZA, ZM, ZW(76) Designated States (regional): ARIPO patent (GM, GM,
KR, LS, MW, MG, SD, SI, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, EG, KZ, MD, RU, TL, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IL, IT, LI, MC, NL, PT, SI, TR), OAPI patent

(Continued on next page)

(54) Title: SYNTHESIS OF SUPERCONDUCTING MAGNESIUM DIBORIDE OBJECTS



(57) Abstract: A process to produce magnesium diboride objects (210) from boron objects (204) with a smaller form. Boron objects (204) are reacted with magnesium vapor at a predetermined time and temperature to form magnesium diboride objects (210) having a morphology similar to the boron object's original morphology.

WO 02/064859 A3

WO 02/064859 A3 

BP, B1, CF, CG, CL, CM, GA, GR, GQ, GW, ML, MO, (80) Date of publication of the international search report:
NE, SN, TD, TG). 10 October 2002

Published:

- with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of refusal of amendment

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT		INTERNATIONAL APPLICATION NO. PCT/US2006/0006
A. CLASSIFICATION OF SUBJECT MATTER IPC(2) : B03D 3/12; C23C 14/10; B01L 9/00 CL CL : C2762.233.26.233.4; B03A30, C34, C04, 473 According to International Patent Classification (IPC) at its last technical classification and IFC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) I.F. : C2762.233.26.233.4; B03A30, C34, C04, 473, 475 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched I.F.A.		
Exhaustive data have been searched during the international search (name of data base used, where practicable, search terms used) EAST SEARCH: access, degradation, Canada, engine, repair, terms		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SHUO KO ET AL., <i>Beam Injector Effect in Superconducting MgB₂</i> , February, 3, 2001, pp. 1-4	1-23
Y	Fineman et al., <i>Thermodynamic and Transport properties of Superconducting MgB₂</i> , February 6, 2001, pp. 4-4	1-23
X	Cutfield, et al., <i>Superconductivity in Doped MgB₂ Wires</i> , February 12, 2001	1-23
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Item C. </div> <div style="width: 45%;"> <input type="checkbox"/> The present family members. </div> </div>		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <input type="checkbox"/> Special categories of prior documents Y = documents defining the present state of the art which is not considered to be of particular relevance X = neither anticipatory nor prior publication or on other the document defining the state of the art Y = documents which have been published or publicly disclosed or which is about to be published, does of earlier documents other than special categories X = documents published by or for the applicant, or the applicant of the invention Y = documents published prior to the international filing date, but after the priority date of the invention </div> <div style="width: 45%;"> Any documents published after the international filing date, however published, that are not in conflict with the applicant's claim to the invention in the language of the language of the invention Documents of particular relevance - the document location, name of the document, date of issue, to be considered to be relevant to the invention in the language of the invention Documents of particular relevance - the document location, name of the document, date of issue, to be considered to be relevant to the invention in the language of the invention Documents of particular relevance - the document location, name of the document, date of issue, to be considered to be relevant to the invention in the language of the invention Documents of particular relevance - the document location, name of the document, date of issue, to be considered to be relevant to the invention in the language of the invention </div> </div>		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> Date of the actual completion of the international search 19 July 2002 (18.07.2002) Name and mailing address of the ISA/US Classification of Patent and Trademark New York Washington, DC, 20540 Headquarters No. (703) 595-1239 </div> <div style="width: 45%;"> Date of mailing of the international search report 20 AUG 2002 Authorized official Richard A. Dillner Telephone No. (703) 595-3775 </div> </div>		

フロントページの続き

(51) Int. Cl. ⁷

F 1

テーマコード (参考)

// C 0 1 G 1/00

C 0 1 G 1/00

S

(81) 指定国 AP (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), EA (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), EP (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OA (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG), AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW

(74) 代理人 100096611

弁理士 宮川 清

(74) 代理人 100098040

弁理士 松村 博之

(74) 代理人 100097744

弁理士 東野 博文

(74) 代理人 100123892

弁理士 内藤 忠雄

(74) 代理人 100100398

弁理士 柴田 茂夫

(72) 発明者 ダグラス・ケイ・フィネモア

アメリカ合衆国 アイオワ州 50014、エイムス、オークランド ストリート 3312

(72) 発明者 ボール・シー・キャンフィールド

アメリカ合衆国 アイオワ州 50010、エイムス、オニックス サークル 806

(72) 発明者 ブドゥコ・エル・セルゲイ

アメリカ合衆国 アイオワ州 50010、エイムス、ブルッドケール サークル 3913

(72) 発明者 ジェローム・イー・オステンソン

アメリカ合衆国 アイオワ州 50014、エイムス、ウェストウッド ドライブ 416

(72) 発明者 セドミール・ベトロビク

アメリカ合衆国 アイオワ州 50014、エイムス、シンクレアー アベニュー 245、アパートメント 308

(72) 発明者 チャールズ・イー・カニングハム

アメリカ合衆国 アイオワ州 50014、エイムス、ピノン ドライブ #108、800

(72) 発明者 ジェラルド・ラベルト

フランス国 グルノーブル F-38000、リュウ ジョルジュ ビゼ 08

Fターム(参考) 4G047 JA03 JA05 JC16 KB04 LB01

4M113 AD36 BA02 CA16

5G321 AA98 CA08 CA18 CA20 DA99

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.